BEAMLINE
X23B

PUBLICATION
M.E. Van der Boom, P. Zhu, G. Evmenenko, J.E. Malinsky, W. Lin, P. Dutta, T.J. Marks, *Langmuir* **18**, 3704 (2002).

FUNDING
National Science Foundation (NSF), ARO/DARPA, Nanovation Technologies, U.S. Department of Energy, Helen and Milton Kimmel Center for Molecular Design.

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Nanoscale Self-Assembly of Thin-Film Molecular Materials for Electro-Optic Switching

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Scientists from Northwestern University in Evanston, Illinois and the Weizmann Institute of Science, Rehovot, Israel, have devised a two-step assembly technique to make highly ordered, intrinsically acentric organic materials which can be integrated into electro-optic (EO) and related devices, such as light modulators and switches. The scientists have shown that the self-assembled photonically/electronically functional materials are competitive in terms of EO responses with the highest efficient polar films reported to date, and are more efficient than inorganic systems, such as $LiNbO_3$.

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Forming nanoscale organic films and integrating them into semiconductor electronics and all-organic microphotonic circuits has stimulated intense academic and industrial research, but progress is hampered by the lack of device-quality functional molecule-based thin films, driving the need for new reliable film-growth methods.

A general applicable method has been developed generating thermally robust multilayered materials. This new synthetic approach involves two alternating deposition steps, as shown in **Figure 1**. First, monolayers (one-molecule-sized layers) of chromophores are covalently bound on hydrophilic substrates (step (i)). The siloxy removal step (ii) renders the surface hydrophilic, thus allowing the rapid build-up of a covalently-bound siloxane-based capping layer. The resulting films are intrinsically acentric, so no post-deposition steps such as high-voltage poling to align the molecular building blocks are necessary, as in other film growth techniques.

We have developed a film growth process based on chemically reliable steps, amenable to automation-by using a single reaction vessel or dip-coating - and allowing an excellent control of material properties - which is of great interest for optical telecommunications and electronic applications. The high degree of control over film dimensions, texture, and properties has been unambiguously demonstrated using various physicochemical analytical tools, including second harmonic generation measurements and synchrotron x-ray reflectivity measurements (XRR) performed at NSLS beamline X23B (**Figure 2**).

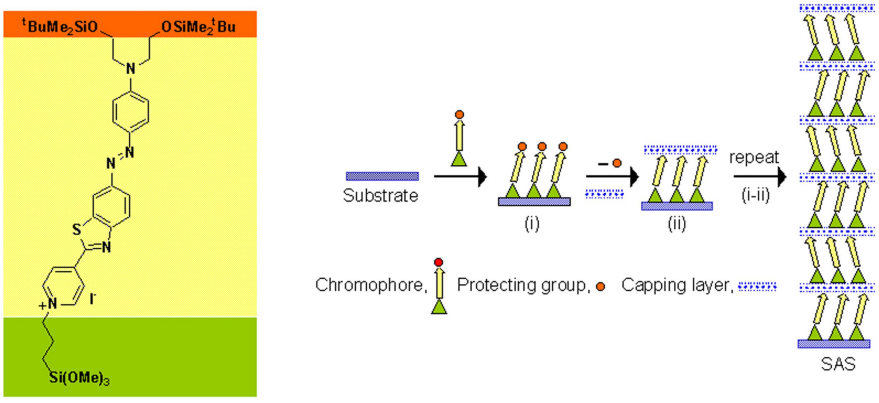

***Figure 1**. Two-step layer-by-layer self-assembly process generating intrinsically acentric superlattices.*

The XRR experiments afforded crystal-clear structural information on the chromophore density (~50 Å²/chromophore), film thickness (~2.8 nm for each chromophore + siloxane-based capping layer), and surface morphology. The robust capping layer is ~8 Å thick. The streamlined two-step assembly process shown in **Figure 1** could be extended to a wide range of molecular building blocks, and become a major synthetic route for the formation of various functional sub-micrometer-sized solids with superb control of material characteristics at the nanoscale level. This assembly process is also part of an ongoing investigation aimed at creating "all-organic" electro-optical modulators (**Figure 3**).

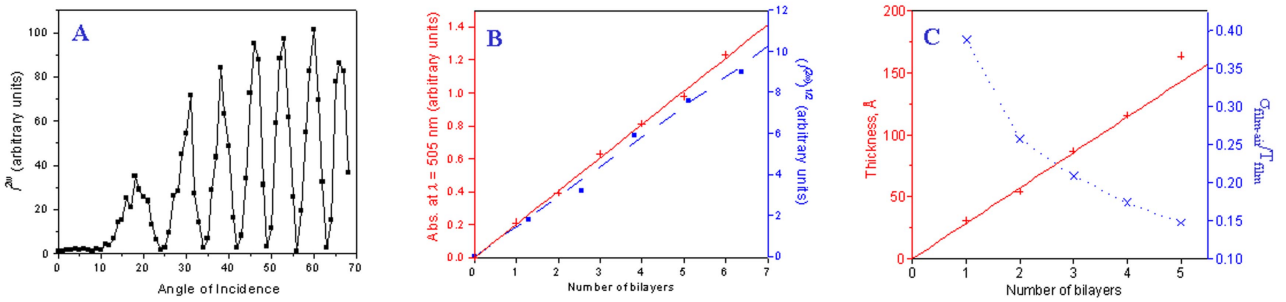

***Figure 2**. (A) Second harmonic generation response at λ_o = 1.06 m as a function of fundamental beam incident angle from a float glass slide having a polar monolayer on either side. (B) Optical transmission and second harmonic generation as a function of the number of bilayers. Left y-axis: absorption at λ_{max} = 505 nm (+). Right y-axis: square root of the SH intensity (•). (C) Specular X-ray reflectivity measurements. Left y-axis: film thickness (Å) as a function of the number of bilayers (+). The solid line is the fit by linear regression for 1-4 bilayers, indicating T = 28.6 ± 0.6 Å × n. Right y-axis: relative film roughness, $\sigma_{film-air}$/T film, as a function of the number of bilayers (×). The dotted line is drawn as a guide to the eye.*

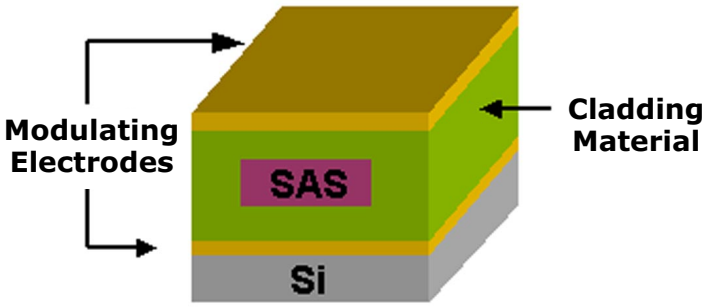

***Figure 3**. Schematic view of a prototype "all-organic" electro-optical modulator based on intrinsically acentric self-assembled superlattices (SAS). Commercially available polymers such as Cyclotene™ and/or Cytop™ can be used as cladding layers.*